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INSTITUTE FOR DEFENSE ANALYSES

## **Technologies for Identifying Munition Fill**

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## **PREFACE**

This document was prepared for the Executive Director of the Environmental Security Technology Certification Program, Office of the Under Secretary of Defense (Environmental Security) and the Technical Director of the Strategic Environmental Research and Development Program under a task entitled "ESTCP/SERDP: Assessment of Traditional and Emerging Approaches to the Detection and Identification of Surface and Buried Unexploded Ordnance."

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## **EXECUTIVE SUMMARY**

### **A. BACKGROUND**

Unexploded ordnance (UXO) detection is typically accomplished using magnetometer or electromagnetic induction (EMI) sensors. The ground near each sensor response is investigated, and scrap, typically the result of ordnance detonations, is separated from intact munitions. At this point, however, the potential hazard of intact munitions is often unknown, and all suspect munitions must be treated as though they present a threat. Although munitions are color coded and marked at the time of manufacture as to their content [e.g., high explosive (HE), illumination, smoke, and training rounds], their condition after years of residence in the ground often degrades to the point where these identification marks are unreadable. A sensor that can determine the contents of munitions would improve the safety and efficiency of UXO cleanup operations. This paper examines various chemical and physical techniques that could provide this capability.

Sensors must be applicable to the "environmental UXO mission," that is, the peacetime cleanup of UXO generated on U.S. ranges by past testing and training. As such, factors that limit applicability to traditional military explosive ordnance disposal (EOD) missions are not necessarily considered an impediment to use of a technology. At the same time, risks that are tolerated by the active-duty EOD community will not be acceptable for the environmental UXO mission. At a minimum, this sensor must work on rounds that have been excavated and can be examined above ground. Even better would be a sensor that could interrogate munitions that had been uncovered but still remained in the ground. We require technologies that can be deployed to the field. The main interest is in the ability to distinguish HE rounds from training rounds, the two most common items in most UXO-contaminated areas. A capability to determine whether fuzes contain primary explosive would also be of interest. Although the quantities of primary explosive tend to be small in comparison to main charges, these compounds are sensitive, and the quantities found in larger rounds could produce significant injuries. The additional ability to identify specific chemical munitions, illumination compounds, smoke compounds, and simulants, while not a requirement, would undoubtedly be an added value.



In this document, we examine field deployability, maturity of the technology, size, weight, power requirements, robustness, speed, cost, and the necessary access to UXO, in addition to the ability of the sensor to detect the target compounds. There is a large body of work in explosives detection, mostly concentrated in applications for mine detection, airport security, environmental monitoring, and forensics. We surveyed various techniques used in these applications for their potential to identify the explosive contents of ordnance.

## **B. CONCLUSIONS**

1. At present, no technique exists for the routine field identification of ordnance fills. X-ray radiographs can and do provide information on the structure of the munition, which can be useful in deducing its contents and condition; however, X rays are not routinely used in UXO cleanups and will not provide definitive identification of chemical composition.
2. Neutron techniques, exploiting either inelastic scattering or thermal neutron capture or both, are promising for determining elemental composition. In tests, these techniques have achieved good success identifying chemical warfare agents and moderate success detecting explosives. The difficulty for explosives identification is the relative insensitivity to nitrogen, which has a small thermal neutron capture cross section and is not a strong, inelastic scatterer of fast neutrons. In addition, detection of nitrogen by means of TNA in soil is hampered by interference from a neighboring Si  $\gamma$ -ray peak. Current efforts may improve sensitivity to nitrogen, however, and should continue. There is no reason at this time to discount neutron techniques for identification of munition fills, including explosives.
3. Data for evaluating acoustic techniques for filler identification are limited but promising. Two systems in development have performed reliably against a limited array of known munitions and fills, with the primary emphasis on detecting chemical warfare agents. More work will be required to explore the applicability of acoustic technology to a wide variety of munitions, with various degrees of damage and degradation, and concentrating on identification of high explosives and inert filler materials.
4. For chemical trace detection, there is a need to establish whether there is a chemical signature for fired, unexploded munitions and to better characterize the background residue in both densely contaminated impact areas and in less

contaminated areas such as safety zones. If the source and background terms are favorable, there is ongoing work to understand the behavior of the explosives in the environment and to develop sensitive techniques for chemical detection. For ease of use, vapor sniffing is the most appealing approach. However, because there is no need to do instantaneous, vapor-phase-only detection for the UXO cleanup mission, it is worth considering the more traditional chemistry techniques used in environmental monitoring and forensic analysis, some of which currently offer very high sensitivity. Since most of the mass fraction of the explosive is sorbed onto the soil, the possibility of detecting analytes in the soil adjacent to the round should not be discounted. In addition, the applicability of swabbing excavated rounds should be explored. For most emerging techniques, ultimate detection limits under field conditions have not been established; this must of course be a priority if source terms are favorable.

## I. INTRODUCTION

### A. BACKGROUND

Unexploded ordnance (UXO) detection is typically accomplished using magnetometer or electromagnetic induction (EMI) sensors. The ground near each sensor response is investigated, and scrap, typically the result of ordnance detonations, is separated from intact munitions. At this point, however, the potential hazard of intact munitions is often unknown and all suspect munitions must be treated as though they present a threat. Although munitions are color coded and marked at the time of manufacture as to their content [e.g., high explosive (HE), illumination, smoke, and training rounds], their condition after years of residence in the ground often degrades to the point where these identification marks are unreadable. A sensor that can determine the contents of munitions would improve the safety and efficiency of UXO cleanup operations. This paper examines various chemical and physical techniques that could provide this capability.

Sensors must be applicable to the "environmental UXO mission," that is the peacetime cleanup of UXO generated on U.S. ranges by past testing and training. As such, factors such as operational tempo or military hardening, which are requirements for applying a technology to traditional military explosive ordnance disposal (EOD) missions, are not necessarily considered essential for a technology to be useful. At the same time, risks that are tolerated by the active-duty EOD community will not be acceptable for the environmental UXO mission and thus, technical performance requirements may be more stringent. At a minimum, we would like this sensor to work on rounds that have been excavated and can be examined above ground. Even better would be a sensor that could interrogate munitions that had been uncovered but still remained in the ground. Although it is not feasible with current technology, the ultimate capability would be the identification of hazardous rounds without any excavation.

We require technologies that can be deployed to the field. Such systems must be sufficiently rugged to operate in real-world, unsheltered conditions, and their size, weight, and power consumption must be compatible with transportation onto a range. However, we also examined technologies that may require off-site processing of samples.

Clearly, this is less desirable than an immediate, local response, but a capability with a high degree of certainty and a turn-around time of hours or even overnight would likely be useful and should not be overlooked.

The Joint Unexploded Ordnance Coordination Office (JUXOCO) has compiled requirements from all of the UXO mission areas, and the ability to determine ordnance fill is identified as a high priority requirement (Ref. 1). No specific performance requirements have yet been generated in terms of probability of correct identification, false positives, or false negatives. It is fairly certain, however, that low false negatives [i.e., incorrect determination that an HE round is safe] will be required for all mission areas, and in particular for the environmental remediation mission. The EOD community is in the process of assembling formal requirements for a filler identification system; the requirements are expected late in 2000. For reference, the EOD requirement for a decision to neutralize an item under current practices is 85/80 (Pd/confidence). The threshold is likely to be at least as high for any instrument discrimination of hazard and will almost certainly be higher yet for the environmental UXO mission.

This document's primary focus is to identify technologies that could determine definitively whether a shell contains HE. The main interest is to distinguish HE rounds from training rounds, the two most common items in most UXO-contaminated areas. A capability to determine whether fuzes contain primary explosive would also be of interest. Although the quantities of primary explosive tend to be small, these compounds are sensitive, and the quantities present in larger munitions could produce significant injuries. The ability to detect spotting charges may also be of interest, particularly for larger rounds, which can contain quantities of black powder in excess of 1 kg. In current practice, munitions suspected of containing a live spotting charge are blown in place. The additional ability to identify specific chemical munitions, illumination compounds, smoke compounds, and simulants would undoubtedly be an added value.

Currently, government EOD technicians make use of mobile X-ray machines to examine recovered rounds. The X rays provide information about the internal structure of the round and type and condition of the fuze. EOD personnel sometimes X ray rounds for intelligence gathering, and they can determine the broad classification of filler, as well as the location and structure of the fuze mechanism. This information is necessary, for example, to determine how to disarm foreign munitions without destroying them. X rays generally are not used to make routine decisions about the disposal method for ordnance for cleanup and range maintenance.

## **B. SCOPE**

In this document, we examined field deployability, maturity of the technology, size, weight, power requirements, robustness, speed, cost, and the necessary access to UXO, in addition to the ability of the sensor to detect the target compounds. There is a large body of work in explosives detection, mostly concentrated in applications for mine detection, airport security, environmental monitoring, and forensics. We surveyed various techniques used in these applications for their potential to identify the explosive contents of ordnance. They can be broadly grouped into physical techniques that detect bulk explosives and chemical techniques that detect trace quantities of filler materials. Before discussing specific technologies, we briefly survey the various munition fill materials that can be encountered.

## II. FILL MATERIALS

Any given weapon system fires a variety of different ammunition for different purposes. For example, the U.S. inventory of 155-mm artillery rounds includes payloads containing high explosives, illumination compounds, smoke/obscurant compounds, incendiary compounds, chemical warfare (CW) agents, and mine/submunition delivery systems, as well as training rounds that can be wholly inert or contain spotting charges. Similar varieties exist for other weapon systems, such as the 105-mm gun, the 60-mm mortar, the 81-mm mortar, and so forth. Table II-1 shows a sampling. These are selected examples only; note that specific content and quantity vary greatly among different models of ammunition, even for the same caliber weapon.

Although there are many potential filler materials, we are most interested in HE. HE shells can contain a variety of energetic compounds, but main charges are primarily TNT, RDX, or mixtures containing one or both of these. Tables II-2 and II-3 list common military explosives and explosive mixtures, respectively. Note that all explosives of interest contain nitrogen, and most have  $-\text{NO}_2$  groups.<sup>1</sup> One exception is black powder, which is used in spotting charges, and which contains nitrogen in the form of an inorganic nitrate salt.

Although the minimum requirement of our sensor does not include identification of specific chemicals other than HE, it is still worthwhile to be aware of other possible fills, noted in Table II-4, that could be encountered, for two reasons. First, some sensors may be able to positively identify other types of shells, either by identifying the fill materials directly or by inference from the physical structure of the shell. Since some of these materials are intrinsically dangerous, this ability could be valuable. Second, for other sensors, fill materials other than HE may confuse the sensors.

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<sup>1</sup> Improvised explosives that contain no nitrogen can be composed of chlorates or other strong oxidizers with energy sources such as sugar. Such compositions, however, are not found in military explosives and therefore are not of interest here.

**Table II-1. Example Payloads of Common Ordnance Rounds (Ref. 2)**

	<b>155-mm Artillery</b>	<b>105-mm Artillery</b>	<b>81-mm Mortar</b>	<b>60-mm Mortar</b>	<b>40-mm Grenade</b>	<b>Bomb</b>
High explosive	6.5–7 kg Comp B or TNT	~ 2 kg Comp B or TNT	0.65–0.95 kg Comp B	154 g TNT or 358 g Comp B	35 g TNT 45 g comp A5	Mk84: 424 kg H-6 or tritonol
Smoke	7 kg WP with about 200 g burster charge (tetrytol or Comp B5)	1.7 kg WP + 113 g tetrytol burster	1.8 kg WP + 36 g tetryl burster	WP + burster charge	0.5 g black powder, 60 g white smoke compound (white dye, $\text{KClO}_4$ , sugar)	74 lb. plasticized white phosphorus
Training	195 g Zn dust, $\text{KClO}_4$ , $\text{KNO}_3$ , Al	M395 = 770 g black powder	25 g black powder	23 g black powder	Smoke, tracer, or flash-bang	M38: 100 lb. sand, 2 lb. black powder spotting charge
Cargo dispersal	51 g M10 expulsion charge with various mine payloads	18 M39 grenades (23.55 g Comp B each)				CBU-87: 202 BLU97 bomb-lets w/287 g cyclotol/Zr each
Illumination*	54 g expulsion charge with ~2 kg illumination compound	315 g black powder; gram-quantities primer; 68 g first fire comp, 0.9 kg illumination compound	1.65 g black powder, 0.4 g primer, 0.6 kg illumination compoundd	227 g illumination compound	1.5 g black powder, 1.0 g primer, 85 g illumination compound	
Chemical	1.2 kg burster charge plus canisters containing DF and OPA which mix to form GB	Primer = 300 g black powder; propellant = 250 g mostly NC; burster = 500 g tetrytol; 0.7 kg GB				BLU-52: 279 kg CS

\* Illumination compound is composed primarily of Mg powder and  $\text{NaNO}_3$ , with laminac. First fire compound is composed of  $\text{KNO}_3$ , laminac, B amorphous 90/92 and pluronic.

**Table II-2. Common Military Explosives**

<b>Explosive</b>	<b>Chemical Formula</b>
TNT	$\text{C}_6\text{H}_2(\text{CH}_3)(\text{NO}_2)_3$
RDX	$\text{C}_3\text{H}_3\text{N}_3(\text{NO}_2)_3$
HMX	$\text{C}_4\text{H}_4\text{N}_4(\text{NO}_2)_4$
PETN	$\text{C}(\text{CH}_2\text{ONO}_2)_4$
Tetryl	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NCH}_2\text{NO}_2$
Black Powder	$\text{KNO}_3$ , S, Charcoal

**Table II-3. Common Military Explosive Mixtures**

Name	Composition
Comp B	TNT/RDX/wax
Comp A-3	RDX/wax
Pentolite	TNT/PETN
C-4	RDX + polyisobutylene+di(2-ethylhexyl) sabacate + fuel oil
A-IX-2	RDX/Al
Tritonal	TNT/Al
Hexal	RDX/Al/wax
Cyclotol	RDX/TNT
Octol	HMX/TNT
Tetrytol	TNT+tetryl

**Table II-4. Examples of Other Substances Found in Munitions**

Name	Chemical Composition	Use
White Phosphorus	P <sub>4</sub>	Obscurant
HC	Hexachloroethane/zinc	Obscurant
Red Phosphorus	P	Obscurant
Sarin (GB)	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> PF	Chemical nerve agent
Mustard (H)	(CH <sub>2</sub> CHCl) <sub>2</sub> S	Chemical blister agent
Illumination Compound	52% Ba(NO <sub>3</sub> ) <sub>2</sub> , 10 % Na(NO <sub>3</sub> ), 26% Al, 5% N <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 4% S, 1% castor oil, 1% linseed oil	Illumination
Illumination Compound	Powdered Mg mixed with an oxidizer (i.e., NaNO <sub>3</sub> )	Illumination
NC/gun cotton	[C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> (ONO <sub>2</sub> )] <sub>n</sub>	Incendiary
Thermite	Iron Oxide and Al	Incendiary
Sand	SiO <sub>2</sub>	Ballast
Antifreeze/water	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Ballast
Concrete		Ballast
Empty		

Training rounds can vary considerably. Some are ballistically matched to their functional counterpart by varying the wall thickness, but are otherwise empty. Most are standard cases filled with various inert materials. There is no standard inert fill; rather, the inert fill material varies, depending on where the round was filled and for what



purpose it was fired. Different fills have been used for practice, for compiling ballistic tables, or for acceptance testing. Of course, the fill will depend on whether the simulated round is HE, smoke, chemical, or cargo dispersal. Reports have documented finding UXO filled with sand, antifreeze, concrete, wax, filler E,<sup>2</sup> and many other compounds or mixtures. Some more exotic fills are used for chemical simulants to match viscosity and density; these include bis-2-ethylhexylmethylphosphonate for VX and dimethylmethylphosphonite for GB. Also, many training rounds contain spotting charges or tracers, which may themselves present an explosive hazard, although a considerably smaller one than a round of the same caliber filled with HE. Most spotting charges contain black powder, which produces flash, an audible report, and smoke. The quantities used in spotting charges vary considerably. Smaller rounds, such as mortars, contain amounts in the 25-g range. Larger items can contain significantly more. For example, the M395 blank 105-mm round reportedly contains greater than 700 g of black powder (Ref. 2). In one operation, spotting charges have been observed to have a dud rate of about 10 percent (Ref. 3).

Other rounds (illumination, obscurant, chemical) contain some HE as a burster or expulsion charge. For some rounds, burster charges are large enough that they may present danger. For example, artillery white phosphorus (WP) rounds contain greater than 100 g tetrytol or Comp B in the burster. In addition, the payloads themselves may be dangerous. WP ignites upon exposure to the air and can set off the burster charge or cause severe burns if it contacts the skin. For chemical rounds the danger is obvious, but most real chemical rounds were fired at known locations.<sup>3</sup>

It is possible that rounds could be identified by the physical characteristics of their structure, in addition to the chemical composition of the fill. For example, illumination rounds carry a canister containing the illumination compound plus a burster charge and a parachute, which should have readily identifiable structures if the interior of the round could be imaged. Similarly, binary chemical rounds contain two canisters bearing the chemical reactants and a burster charge. Cargo rounds contain grenades or mines, whose structures may be discernable. Currently, in limited circumstances, X-ray techniques are used for examining the internal structure of munitions.

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<sup>2</sup> The authors have not determined the makeup of Filler E.

<sup>3</sup> Nevertheless, there are examples of chemical munitions having been found in forgotten locations. For example, in 1992 the Spring Valley section of Washington, D.C., was found to contain chemical ordnance from WWI experiments at American University.

### III. DETECTION OF BULK EXPLOSIVES

#### A. NEUTRON TECHNIQUES

When neutrons interact with nuclei, a  $\gamma$ -ray spectrum is produced that allows the nuclei to be identified. Gamma rays are produced by two types of neutron reactions: neutron capture and inelastic scattering.<sup>4</sup> When a neutron is captured by a nucleus with  $A$  nucleons, a compound nucleus with  $(A+1)$  nucleons is produced in an excited state. That excited nucleus then de-excites, emitting one or more characteristic  $\gamma$  rays, depending on whether it de-excites directly to the ground state or through intermediate energy levels. Neutron capture cross sections increase as the neutron energy decreases; hence, neutron capture occurs primarily with thermal neutrons. Inelastic scattering results when a high-energy neutron (or fast neutron) collides with a nucleus  $A$ , leaving it in an excited state  $A^*$ . That excited nucleus then de-excites, emitting a  $\gamma$  ray characteristic of the nucleus  $A$ . Inelastic scattering always involves a neutron threshold energy that depends upon the energy level structure of the target nucleus (i.e., the neutron must have enough energy to excite the target nucleus to a higher energy level).

Whether a nucleus can be detected using neutrons depends in part upon the neutron source. Radioisotopic sources such as  $\text{Cf}^{252}$  produce a fission spectrum of neutrons peaked at about 1 MeV, with an average energy of about 2 MeV. Although the spectrum does have a high-energy tail extending out to almost 20 MeV, most of the neutrons produced have energies of not more than a few MeV. This limits inelastic scattering interactions to those nuclei with energy levels less than a few MeV above the ground state. For example, oxygen and carbon cannot be detected with a  $\text{Cf}^{252}$  source; their thermal neutron capture cross sections are far too low, and they cannot be detected by means of inelastic scattering because the neutron threshold energies are 6.4 MeV and 4.8 MeV, respectively. A deuterium-tritium neutron generator (or D-T tube), on the other hand, produces 14 MeV neutrons, which have sufficiently high energy to inelastically excite most nuclei. However, neutron capture interactions will be rare with a D-T tube

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<sup>4</sup> A third possible source of  $\gamma$  rays is radioactive decay resulting from the activation of certain nuclei by neutrons. In general, however, this interaction is less important than the two discussed here.

unless a significant amount of moderator is used to slow the neutrons down.<sup>5</sup> Of course, the choice of neutron source is not driven solely by the desired neutron energy.  $\text{Cf}^{252}$  sources are very reliable and long lived and significantly less expensive than D-T tubes.  $\text{Cf}^{252}$  sources typically cost about \$3,000 and last 2 to 3 years, while D-T tubes can cost \$90K or more and have lifetimes of a few thousand hours at most.<sup>6</sup>

It should be noted that this particular application of neutron analysis, where the munition can be interrogated above ground, is considerably simpler than that of buried explosives detection, where background counts due to neutron interactions with various soil elements generally dominate the signal. Nonetheless, background is still a concern in this application, although much less so. Specifically, background radiation is generated by neutron interactions in the detectors, as well as in the munitions casings.

In general, performance will be limited by the time available to make measurements and by the size of the munitions being interrogated. Details of four different neutron identification techniques are discussed below.

### 1. PINS Chemical Assay System

One approach to neutron identification of fill material is the portable isotopic neutron spectroscopy (PINS) system developed jointly by EG&G Ortec and the Idaho National Engineering and Environmental Laboratory (INEEL), which exploits both neutron capture and inelastic scattering interactions. This system uses a 5- $\mu\text{g}$   $\text{Cf}^{252}$  neutron source that emits about 10 million neutrons per second and 40-percent relative efficiency high-purity germanium (HPGe) detectors,<sup>7</sup> which produce high-quality spectra that allow for easy discrimination between close-lying  $\gamma$ -ray peaks of different chemical elements. A complete PINS system weighs about 500 lb and costs about \$100K. The individual components of the PINS system are light enough that they can be assembled by one person. PINS is currently field deployable; its principal customer is the U.S. Army Tech Escort Unit, which most often encounters munitions filled with CW agents and obscuring smoke chemicals.

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<sup>5</sup> A reflector could be used to force the neutrons to make multiple passes through the material. The neutrons will lose energy through collisions with the light elements in the material, eventually becoming thermalized.

<sup>6</sup> On the other hand, there are hidden costs associated with radioisotopic sources. In addition to shielding, there are costs associated with acquiring a license to use a radioactive source, paperwork processing every time the source must be shipped, and disposal costs, which can be greater than the purchase price.

<sup>7</sup> This efficiency is relative to a 3 in.  $\times$  3 in. NaI detector at 1.332 keV.

Between 1992 and 1997, PINS was tested on 130 suspect munitions and containers. Count times were about 20 min per item. Details of the results can be found in Reference 4. Tables III-1 and III-2 are reproductions of Tables 6 and 10, respectively, in Reference 4.

**Table III-1. Table 6 from Ref. 4: PINS Accuracy by Verified Fill Classification**

Verified Fill	Correct ID	Total	% Correct
CW agent	38	41	93
empty	12	12	100
explosive	0	9	0
simulant	35	35	100
smoke	15	15	100
other	6	17	35
Total	107	130	82

**Table III-2. Table 10 from Ref. 4: Incorrectly Identified Munitions**

Location	No.	Type	Key Elements	PINS Result	Direct Sampling Result
Edgewood	1	4.2-in. mortar	Cl	suspect HD (mustard gas)	dichlorobenzene
N-Field, April 1994	1	155 mm	weak P	possible GB	P, Mg salts
	3	175 mm	P	GB	VX
Edgewood	9	75 mm	NKE <sup>a</sup>	empty	nitrobenzene/aniline
King's Creek, October 1994	9	75 mm	NKE <sup>a</sup>	empty	TNT

<sup>a</sup> No key elements detected.

These test results indicated two shortcomings of the PINS system. First, its relatively low sensitivity to sulfur resulted in three 175-mm projectiles being classified as containing GB (sarin), when in fact, they contained VX. (VX contains sulfur, but GB does not.) Sulfur is identified by a 2.233-keV inelastic scatter  $\gamma$  ray. After these results were obtained, the neutron source was moved from the center of the polyethylene moderator block to its edge nearest the test item. This reduced the impact of the moderator, resulting in an increased flux of fast neutrons on the test item, and hence an increased production of inelastic scatter  $\gamma$  rays. This enhancement also improved the system's sensitivity to phosphorus, arsenic, and titanium inelastic  $\gamma$ -ray peaks.

Second, the PINS system was insensitive to nitrogen, incorrectly classifying nine TNT-filled 75-mm projectiles as empty (see Table III-2). Although nitrogen emits an easily distinguishable 10.8-MeV capture  $\gamma$  ray, its thermal neutron capture cross section is very small.<sup>8</sup> Furthermore, 75-mm projectiles are relatively "small," containing about one-fifth the explosive in 155-mm projectiles. Unfortunately, the nine 75-mm projectiles were the only items out of the 130 tested that contained TNT, so it is not possible to know how much nitrogen needed to be present for TNT to be detected.<sup>9</sup> INEEL ran some tests with simulated 75-mm projectiles and determined that 50- to 80-min counting times were necessary to detect TNT in these munitions reliably. (Recall that for all results presented above, 20-min measurement times were used.)

To improve PINS sensitivity to nitrogen, particularly in small items, INEEL has designed a graphite neutron reflector annulus that surrounds the test item. In the standard PINS system, neutrons that pass through the test item without interacting are lost. A reflector surrounding the test item allows for multiple passes of the neutrons through the munition, increasing their probability of interaction. The reflector material must have a very low neutron capture cross section, making graphite one obvious choice. Aluminum and beryllium are also being considered. Preliminary results in the lab indicate a decrease in counting time by a factor of 3 using graphite for 75-mm projectiles; Monte Carlo simulations suggest that beryllium may result in a factor of 4 to 5 decrease in counting times.<sup>10</sup>

Another possible solution would be to design the system to have insertable moderating elements, so that the neutron energy entering the test item can be tuned. For example, using very little moderator would optimize the system for inelastic scattering reactions, which would be useful for CW agent identification. A significant amount of moderator would tune the system for thermal neutron capture interactions, thereby optimizing it for HE detection. When asked about the possibility of implementing such a "tunable device," Dr. Caffrey reported that the engineers at INEEL have found that by moving the neutron source to various positions inside the moderator block, they can vary the thermal neutron flux at the test object by 25–50 percent. Note that for a "tunable

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<sup>8</sup> The total thermal neutron capture cross section is only 0.08 b. Furthermore, the cross section for the de-excitation directly to ground, which produces the 10.8 MeV  $\gamma$ -rays, is only 0.011 b.

<sup>9</sup> Note that the count rate (or sensitivity) will not increase linearly with nitrogen content because of the self-screening effects due to competing reactions that scavenge the neutrons, particularly  $N^{14}(n,p)$ , which has a 1.77 b cross section. (See Ref. 2.)

<sup>10</sup> Source: email contact with Dr. Caffrey at INEEL.

PINS," it would not be necessary to know ahead of time whether the fill is likely CW or HE. For example, two PINS systems in series, one tuned for thermal neutron interactions and the other for fast neutron interactions, could be used. The disadvantage of this approach, however, would be measurement time. This system requires about 20 min per item (without a reflector), so the total measurement time would be at least 40 min per item. (Also, using two PINS systems implies twice the cost of one system.) On the other hand, one may have a good idea whether HE or CW fill is likely to be encountered, and thus, only one "properly tuned" system may be necessary.

A miniPINS system that will weigh about 80 lb. is currently under development. The weight reductions are primarily the result of improved mechanical design. The amount of shadow-shielding and moderator materials has been greatly reduced, from about 70 to about 18 lb., and the lighter shielding permits a lighter support table for the detector. Also, the electronics package has been reduced from 25 to 5 lb. The number of shipping boxes will be reduced from five footlocker-sized containers to only one.

## **2. PELAN System**

The Pulsed ELemental Analysis with Neutrons (PELAN) system was developed by Dr. G. Vourvopoulos of Western Kentucky University (Ref. 5). PELAN uses a pulsed D-T neutron generator, which has a neutron pulse duration of a few microseconds and a pulse frequency of a few kilohertz. Bismuth germanate (BGO) scintillation detectors are used to detect the  $\gamma$  rays. As with the PINS system, PELAN attempts to exploit both neutron capture interactions and inelastic scattering interactions. Unlike the PINS system, however, this system can detect the presence of both carbon and oxygen, because it uses a 14-MeV neutron source. The pulsed source allows for isolation of the fast and thermal neutron interactions. To be specific, during the fast neutron pulse, the  $\gamma$  rays generated by fast neutron interactions on C, N, and O are measured. When the neutron beam is off, the fast neutrons thermalize, and the capture  $\gamma$  rays generated by thermal neutron interactions with H, N, and Cl are measured.

This system has been tested at the proof-of-principle level in a laboratory setting. Several 105-mm projectiles were obtained from the Jefferson Proving Ground. The empty projectiles were filled with chemical materials that had the same elemental composition as the high explosives. Two separate tests were conducted in which personnel placed the projectiles at random in front of the detector. Each object was interrogated for 10 min. The PELAN system was able to identify the contents of each

munition placed in front of it. Dr. Vourvropolous is planning to conduct more detailed tests for the FBI in the near future.

### 3. PFNA

Pulsed fast neutron analysis (PFNA) was developed by SAIC for automated cargo inspection (Refs. 6–8), as an improvement over fast neutron analysis (FNA). FNA attempted to exploit inelastic scattering reactions off of C, N, and O, but it suffered from very high background radiation stemming primarily from interactions of scattered fast neutrons with detector materials. These detectors could not be adequately shielded without sacrificing their efficiency. The idea behind PFNA is to separate the neutrons from the stimulated  $\gamma$  rays in time because the fast neutrons are slower (3.9 cm/ns for 8 MeV neutrons, 5.2 cm/ns for 14 MeV neutrons) by about a factor of 7 than the speed of light (30 cm/ns). This requires that the neutrons be monoenergetic so that faster neutrons do not reach the detector and interfere with  $\gamma$  rays stimulated by slower neutrons. Furthermore, the neutrons must be bunched in narrow pulses, relative to the flight time across the test object, so that all of the stimulated  $\gamma$  rays arrive at the detector before the neutron pulse does. PFNA therefore uses nanosecond pulsing, which provides a three-dimensional image of all the elements that yield a significant production of distinguishable  $\gamma$  rays using time-of-flight (TOF) analysis to identify the positions of the interactions.

The current PFNA system uses a deuteron accelerator to generate 5–6 MeV deuterons which interact with a  $D_2$  gas target to produce 8–9 MeV neutrons by means of the  $d(D,n)He^3$  reaction. These high-energy neutrons produce inelastic scatter  $\gamma$  rays off of C (4.43 MeV line), O (6.13 MeV line), and N (5.11, 2.31, and 1.64 MeV lines<sup>11</sup>).

SAIC has built a fully operational prototype of a PFNA system at its Santa Clara Laboratory. PFNA has not yet been used to identify munition fill, but the application to cargo inspection is similar enough that the transition should be straightforward.

### 4. TNA

Thermal neutron analysis (TNA) is limited to thermal neutron capture reactions, and in the case of explosives, TNA focuses on the detection of nitrogen by means of the  $N^{14}(n,\gamma)$  reaction, which produces 10.8 MeV  $\gamma$ -rays. TNA has been used in this manner in

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<sup>11</sup> The 1.64 MeV line is the result of the production of  $N^{14}$  in an excited state 3.95 MeV above ground, which de-excites to the first excited state at 2.31 MeV above ground.

the detection of buried explosives in ordnance and landmines with some success (see Refs. 9 and 10). Unlike that application however, the signal in the nitrogen window in this application is not dominated by a competing soil reaction on  $\text{Si}^{29}$ , which produces 10.6-MeV  $\gamma$  rays.<sup>12</sup> There will still be background radiation generated by both pile-up and neutron capture in the detectors, but this should be less of a concern than for the fast neutron applications described above, because the window of interest is at very high energy. If a  $\text{Cf}^{252}$  source is used, contamination to the nitrogen window from pile-up of  $\gamma$  rays produced by fast neutron interactions should be small because most of the neutrons will not have sufficient energy to produce high-energy, inelastic-scatter  $\gamma$  rays. Pile-up will be produced from thermal capture  $\gamma$  rays off of elements in the munitions casing, especially  $\text{Fe}^{54}$  (5.9 percent of naturally occurring iron), which produces a 9.3-MeV  $\gamma$  ray, and  $\text{Fe}^{56}$  (91.72 percent of naturally occurring iron), which produces a 7.65-MeV  $\gamma$  ray. If a D-T neutron generator is used, pile-up will become a serious concern because of fast neutron interactions, but pulsing the source should mitigate that effect.

TNA is not limited to nitrogen detection. Chlorine, which is present in both mustard gas and lewisite, has an extremely large (n, $\gamma$ ) cross section (in excess of 40 b) and emits a 6.11-MeV  $\gamma$  ray. Sulfur, present in VX, has an (n, $\gamma$ ) cross section of 0.53 b and emits a 5.42-MeV  $\gamma$  ray. Hydrogen, present in all explosives, has an (n, $\gamma$ ) cross section of 0.33 b and emits a 2.2-MeV  $\gamma$  ray. Nonetheless, the number of detectable elements is limited to those with significant capture cross sections; C and O, for example, cannot be detected because their thermal neutron capture cross sections are far too small. On the other hand, almost all of the isotopes currently detected by PINS by means of inelastic scattering (P, As, Ti, Si, Cl, H, N, and S) can in principle be detected using TNA instead.<sup>13</sup> Only boron, which is used as an identifier of antifreeze (sometimes used in practice chemical munitions) cannot be reliably detected with TNA, because  $\text{B}^{11}$ , which is 80 percent of naturally occurring boron, has a very small capture cross section (5 mb),

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<sup>12</sup> Practice munitions are sometimes filled with sand, which could present a problem, particularly if scintillation detectors such as NaI are used, because they cannot resolve the 10.6-MeV  $\gamma$  ray generated from  $\text{Si}^{29}$  and the 10.8-MeV  $\gamma$  ray generated from  $\text{N}^{14}$ .  $\text{Si}^{29}$ , however, is only 1.6 percent of naturally occurring silicon, so the 10.6-MeV  $\gamma$  ray will be a weak signal. The reason that  $\text{Si}^{29}$  is such a problem for the detection of buried explosives is that the size of the target is very small relative to the amount of sand that is irradiated around it.

<sup>13</sup> The (n, $\gamma$ ) cross sections and associated neutron binding energies are as follows: P: 0.166 b, 7.935 MeV; As: 4.5 b, 7.326 MeV;  $\text{Ti}^{48}$  (73.72 percent of naturally occurring Ti): 7.843 b, 8.142 MeV;  $\text{Si}^{28}$  (92 percent of naturally occurring Si) 0.177 b, 8.474 MeV. Each isotope typically has several  $\gamma$  rays associated with its de-excitation; those  $\gamma$  rays resulting from de-excitation directly to the ground state will have energies equal to the neutron binding energy. The most probable de-excitation, however, is often through several intermediate steps, which yield lower energy  $\gamma$  rays.



and  $B^{10}$ , which is 20 percent of naturally occurring boron, is about 8 times more likely to produce an  $\alpha$  particle than a  $\gamma$  ray when it captures a thermal neutron. It is interesting to note that the developers of PINS originally thought that thermal capture reactions alone would provide sufficient information. They discovered, however, that the inelastic reactions were more favorable for certain isotopes (e.g., As, P, and Ti). Calculations indicated that thermal neutrons suffer much greater scattering losses than fast neutrons in the steel walls of munitions. Furthermore, for some isotopes, the probability of de-excitation yielding relatively high energy  $\gamma$  rays (i.e. the branching ratio) is small.<sup>14</sup> The PINS developers therefore opted to irradiate test objects with both thermal and unmoderated  $Cf^{252}$  neutrons. Nonetheless, it is not clear that TNA should be ruled out at this time.

## 5. Neutron Summary

There are two general approaches to using neutrons in fill identification. The first approach is to try to exploit both thermal neutron capture and inelastic scattering reactions. This is the approach taken by both PINS and PELAN. The major difference between the two systems is the type of neutron source employed. PINS currently uses a  $Cf^{252}$  source, which excludes detection of C and O, and PELAN uses a D-T source, which allows for the detection of both C and O. On the other hand,  $Cf^{252}$  produces less background radiation from fast neutron interactions, and it is a much more reliable and inexpensive than a neutron source. It is difficult to compare the two systems because PELAN has not been tested at nearly the level as PINS. Furthermore, both systems are still evolving; for example, INEEL has recently purchased a D-T neutron generator and intends to do extensive testing to determine whether such a source will significantly improve the performance of PINS.<sup>15</sup>

The second approach is to use either thermal neutron capture reactions or fast neutron scattering interactions. TNA is an example of the former, PFNA an example of the latter. The major drawback of TNA, which may limit its usefulness, is its inability to detect some elements, especially C and O. PFNA, by focusing only on fast neutron scattering, can employ a very short neutron (ns) pulse and eliminate background contributions from neutron interactions in the detectors. PFNA also uses TOF

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<sup>14</sup> For example, in the case of P, the most intense capture  $\gamma$  ray is a 3.9-MeV transition with a 15-percent branching ratio.

<sup>15</sup> If INEEL does choose to use a D-T source, the PINS price will nearly double.

measurements to obtain high-quality, three-dimensional images. The focus of PFNA thus far has been on automated inspection of large cargo, but there is no obvious reason why it cannot also be used for identifying munition fill.

The only way to quantify the benefits and limitations of neutron detection techniques is to conduct a set of independent and thorough tests. It is not sufficient to rely on "blind tests" conducted in a laboratory setting by the developers of the different systems. Until such objective tests are conducted, the only conclusion that can be drawn is that these approaches seem reasonable, and there is no reason at this stage to discount their utility in the area of fill identification.

## **B. X RAY**

X rays, which are photons in the range of roughly 1 keV to 1 MeV, can be used to probe the internal structure of objects. This is typically accomplished by measuring the transmission of the X rays through an object. The best known applications of X-ray imaging are in the health care (medical and dental) and nondestructive testing industries, but the technique is also applied to probing the internal structure of UXO items.

Photons in the X-ray band interact more strongly with objects containing high-Z atoms, where Z is the atom's atomic number (or nuclear charge). Hence, the X rays will be absorbed more readily by an object rich in iron, compared with an object rich in carbon, nitrogen, or hydrogen. This is why an amalgam filling in a tooth stands out in a dental X ray: the filling, made of high-Z metal, absorbs the X rays much more than the tooth tissue, which contains low-Z elements, does. The result is an image that shows excellent contrast between the filling and the tooth.

Although X rays are sensitive to Z, it is not possible to accurately determine the chemical makeup of the item being imaged. Instead, images of an object's mechanical structure can be created. Understanding the mechanical structure of UXO can be a great help in understanding whether the round is inert or dangerous. For example, an unexploded HE round could contain structures including a fuze, a booster charge, and a main charge. A practice round filled with an inert material such as cement may not contain the same sort of internal structure as live ordnance. These structural differences can be detected by X-ray radiography. Further, the main charge in a live round is typically homogenous (such as cast TNT). Cement is not a particularly homogenous material; hence, the cement may display a grainy image compared with an explosive material. On the other hand, X-ray lithography may not be sufficient to determine if a round is inert. For example, chemical and smoke rounds may contain a canister and a

burst tube that disperses the chemicals contained in the round. A practice chemical round may have the same physical structure as a live round—a canister of liquid (antifreeze) and a burst tube—even though the tube is not needed in the practice round. In general, however, the structural information revealed by X-ray radiography can be useful in understanding the UXO filler. X rays may also be especially sensitive to primary explosives in the fuze. Many of these compounds, including mercury fulminate ( $\text{Hg}(\text{ONC})_2$ ), lead azide ( $\text{Pb}(\text{N}_3)_2$ ), and lead styphnate ( $\text{PbC}_6\text{H}_7\text{N}_3\text{O}_8$ ), contain high-Z atoms.

X-ray radiography equipment consists of an X-ray source and a detector placed on opposite sides of the UXO object. The transmission of X rays through the UXO is recorded on the detector. The X-ray source can either be an active X-ray device or a radioactive source such as cobalt ( $^{60}\text{Co}$ ): Active X-ray sources can be turned on and off, and they are typically available at moderate X-ray energies that are useful for medium-sized UXO. A cobalt source provides X rays in excess of 1 MeV, useful for penetrating large, thick-walled UXO such as 155s. Radioisotopic sources, of course, cannot be turned off, so they require shielding when not in use. Detectors are typically made of light-sensitive film, but there is a move in radiography towards detecting the X rays with charge-coupled device (CCD) arrays. Film requires processing to view an image, but a CCD image has the advantage that it can be seen immediately after the item is exposed to the X rays. Radiography equipment is reasonably portable, and it can be used in the field so long as enough soil is removed from around the UXO so that a transmission measurement can be made.

### C. ACOUSTICS

Attempts have been made to differentiate filler materials based on their bulk acoustic signatures. In experiments at INEEL, a broadband acoustic signal (white noise from an ordinary loudspeaker) was used to induce vibrations in munitions. An 85-dB signal in the range 800 Hz to 17 kHz generated natural resonance modes on the surface of the object. These were measured with a laser vibrometer. The density, viscosity, and elasticity of fill influence the signature, that is, the frequencies and amplitudes of resonances. The filler compound is deduced by matching observed spectra to library of known munitions. Both the loudspeaker and the laser vibrometer are commercially available. The data collection takes 12 sec per munition. The laser measurement is done from standoff, while the speakers are positioned about 1 ft from the munition (Ref. 11).

INEEL has tested 155-mm shells containing various chemical warfare agents, chemical simulants, and obscurant compounds, including WP, GB, VX, H, GB-S, VX-S, H-S, sand, and ethylene glycol. On a limited data set, 98 percent of samples were classified correctly. Difficulties were encountered differentiating real VX agent from VX-S simulant (Ref. 11). No tests were done on HE rounds.

Under sponsorship of the Defense Threat Reduction Agency (DTRA), Los Alamos National Laboratory has developed the Swept Frequency Acoustic Interferometer (SFAI) in support of implementation of the Chemical Weapons Convention (Ref. 12). The system is a modified commercial off the shelf instrument from Nick Electronics. Two wideband piezoelectric transducers are placed in mechanical contact with the item to measure its acoustic response in the 1- to 10-MHz frequency range.

The SFAI has been tested against a variety of liquid chemical agents and high explosives in artillery and mortar projectiles. With response times of 1 minute, reliable performance has been reported, with 90-percent correct identification of some munitions at 90-percent confidence. However, in its current form, the system matches responses of unknowns to a library of signatures and requires prior knowledge of the container geometry.

#### **D. NUCLEAR QUADRUPOLE RESONANCE**

Emerging results indicate that nuclear quadrupole resonance being developed by Quantum Magnetics, Inc., of San Diego, California, will be a powerful technique for the detection of bulk explosives for airport security and landmine detection. The pure quadrupole transitions of nitrogen are driven by an oscillating magnetic field with a frequency of about 1 MHz, which must penetrate the explosives. Ordnance constructed of steel, however, is not a candidate for interrogation by this technique because the necessary oscillating magnetic field cannot penetrate the casing.

## IV. CHEMICAL TECHNIQUES

By chemical techniques we refer to techniques that sense trace quantities of filler chemicals that may be present in the surrounding environment. These samples could be present in vapor emitted from the round, in the soil surrounding the munition, or perhaps on the surface of the munition from contamination at the point of production. This has been an active area of research for mine detection within the DARPA dog's nose program, but little is known about the possible chemical signatures of UXO. Under SERDP funding, Sandia National Laboratory has performed experiments on a small number of munitions. The chemical techniques discussed below do not constitute an exhaustive list of potential explosives detectors. Our survey does, however, include techniques from traditional analytical chemistry and from innovative research, and it gives an indication of the achieved and potential detection limits for comparison to available sample quantities when they are determined.

The explosives detection application most closely resembling UXO identification is mine detection, where there is an ongoing DARPA program to detect mines using their chemical signatures. The UXO problem is operationally less stressing than mine detection. For rate of advance, mine detection requires an instantaneous response above the earth's surface if the chemical signature is to be used as a primary detector. For UXO, which could be detected by other means (magnetometer or EMI) and uncovered, direct access to the ordnance item is possible. Further, while faster is undoubtedly better, there is no need for an instantaneous response: a sensor with a response time of a few minutes is undoubtedly of added value, and even responses that could be had overnight may be useful. On the other hand, detecting explosives inside of UXO by an external trace chemical signature is likely to be more challenging technically than the parallel task for mine detection. Most ordnance items are constructed of a several-millimeter thickness of steel, rather than the thin plastic or metal mine casings, and considerably less sample is likely to be available.

Compared to other explosive detection applications, UXO is much dirtier than airport security screening. However, it may be comparable to environmental monitoring of soil contamination or forensic testing to discern the makeup of a bomb from unexploded residues. These applications require that a signature be extracted from

a complex matrix of soil or debris. For both of these applications, traditional chemistry techniques, such as solvent extraction followed by high-performance liquid chromatography (HPLC) or ion mobility spectroscopy (IMS), are often used. These techniques may be acceptable for the UXO identification mission if there is a trace signature available for UXO. It seems possible to swab a shell, as briefcase handles are swabbed in airport security, or to do solvent extraction of soil surrounding a shell to obtain a needed chemical sample. These samples could then be analyzed using a variety of chemistry techniques. One possibility would be to collect a whole field full of such samples for overnight processing in a nearby laboratory.

## **A. TRACE SAMPLE ISSUES**

### **1. Sample Availability**

The success of any chemical technique intended to sense trace quantities of explosives will depend upon the availability of a chemical sample associated with ordnance and distinguishable from background contamination. Both the quantity and composition of this potential sample, as well as the level of background contamination for UXO sites, are largely unknown. To date, there has been little study of the source term from UXO. Ongoing work investigating vapor availability in mine detection has produced results which may provide an upper bound for the expected sample available from UXO. Although there has been a great deal of work on soil detection of explosives at ordnance plants, it has been directed toward contamination from manufacture or load-and-pack (LAP) operations; there is little data about contamination from exploding, unexploded, or intact buried ordnance.

We assert that the chemical signature available from a mine represents the upper bound for ordnance because the material and construction of shell casings should be more difficult to penetrate than mine casings. Most ordnance is encased in steel several millimeters thick. Although many types of rounds have threads where fuzes are inserted, which could provide a pathway for sample migration, many other rounds exhibit considerable structure between the fuze and the main charge, which would inhibit transport through this pathway. It is possible that damage to the round during impact would provide a pathway for sample migration, but the effects of impact are currently unknown and cannot be presumed to be a reliable source of trace samples. Some contamination from mines is hypothesized to be due to residue from the manufacture and handling that sticks to the outside of the case. If this hypothesis is correct and

contamination is present for ordnance, it is uncertain how this residue would survive the trip through the gun barrel upon being fired or how long initial contamination, unreplenished by a constant leak, would persist in the environment.

There is some question about which chemical compound should be the target analyte of a chemical sensor. It is unlikely that the best results will come from simply detecting the principle HE fill compound (i.e., TNT, RDX, HMX). For example, it is thought that TNT may be more easily be detected through associated manufacturing impurities or breakdown products that have greater environmental availability. Thus, two isomers of DNT, nitrotoluenes, nitrobenzenes, and the biodegradation aminonitrotoluene products are all candidate analytes. From environmental monitoring of TNT contamination at LAP facilities, it is known that all these compounds are found in varying quantities. Because DNT has a substantially higher vapor pressure, head space concentrations (i.e., vapor phase sample available) are about 8 times greater for DNT than for TNT.

Experimental results of trace quantities of explosives available from buried mines point to sample availability in the low part per billion range at best (1 ppb = 1 µg/kg). Generally, explosives have low vapor pressures and low water solubilities. Table IV-1 lists these parameters, as well as the boiling points, for some compounds of interest (Ref. 13). Initial results of models show that in the complex soil environment, 90 percent of the mass fraction of TNT is sorbed onto soil, 10 percent is in aqueous solution, and a negligible amount (down by several orders of magnitude) is found in the soil vapor phase (Ref. 14). This points to the difficulty in using chemical detection of explosives. The most convenient source from a sampling perspective would be the vapor phase, which represents by far the smallest mass fraction of explosive. Solid sampling could take the form of either sampling the soil surrounding the munition, in which the greatest mass fraction of sample is found, or swabbing the exposed item for surface contamination.

**Table IV-1. Physical Properties of Common Military Explosives (Ref. 13)**

Compound	Vapor Pressure (torr)	Aqueous Solubility (mg/L)	Boiling Point (°C)
TNT	$1.1 \times 10^{-6}$	130	240 (explodes)
TNB	$2.2 \times 10^{-4}$	385	315
2,4-DNT	$1.4 \times 10^{-4}$	270	300
Tetryl	$5.7 \times 10^{-9}$	80	Decomposes
RDX	$4.1 \times 10^{-9}$	42	Decomposes
HMX	$3.3 \times 10^{-14}$	5	Decomposes

In one experiment, explosive quantities in soil surrounding a mine were measured using solvent extraction followed by IMS.<sup>16</sup> Immediately after burial, concentrations were mostly below detection limits (0.4 ppb for TNT and 7.4 ppb for RDX). But after 10 months of burial, the explosive level in soil increased to 8 ppb for TNT (Ref. 15). Vapor measurements using radio-labeled TNT indicated subpart per trillion (ppt) concentrations inside and near minefields (Ref. 16). However, this study did not look for local "hot spots" over individual mines, which would be expected to contain higher vapor concentrations. Head space vapor concentration of TNT in lab experiments has been found in the parts per billion range, but even in highly controlled laboratory conditions, vapor availability of less volatile explosives, such as RDX, will be orders of magnitude lower. Surface contamination for mines has been found in one experiment to average 15 ng/cm<sup>2</sup>, with wide variation (Ref. 17). For one model, the rates of release (for two mines studied) were found to be 10<sup>-16</sup> to 10<sup>-18</sup> g/cm<sup>2</sup>-sec (Ref. 18). The same study shows no significant change in the flux results if the release term (diffusion through the case) is set to zero. This suggests that initial surface contamination, if present, may be the dominant contributor to the chemical signature.

Under SERDP sponsorship, Sandia National Labs has examined the surface contamination of a small number of ordnance items (Ref. 19). The study included both training practice (TP) and high explosive (HE) filled rounds that had never been fired. Chemical analysis of methanol-removable residue indicated that for all three types of ordnance (60-mm mortar, 81-mm mortar, and 105-mm artillery), quantities in excess of 1 µg of TNT, DNT, TNG, and RDX were found for both the TP and HE rounds. When the paint was removed from an 81-mm mortar and analyzed, more than 25 µg/g of TNT was found and several µg/g quantities of DNT, Am-DNT, and RDX were seen as well. Of course, this work addresses only initial contamination levels, and more tests will be required to quantify the effects of firing and residence in the ground on surface contamination. Nevertheless, the substantial contamination observed on the TP rounds suggests that using trace chemical means to identify HE rounds may be problematic. After the experiments, however, it was discovered that the TP rounds used in these tests were likely former HE-filled rounds that had been through a demil process and were then to be reused as TP rounds. It is thus difficult from these experiments to make general comparisons of contamination on TP and HE rounds.

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<sup>16</sup> See section below for a discussion of IMS.



The behavior of explosives in the environment is complex. Their chemical fate in the environment is an active area of research, but it is currently poorly understood, especially at the concentration levels of interest for trace signature detection. One requires a knowledge of and the ability to model low concentration chemical and physical properties of the molecules in question. There are many important factors, including sample origin, phase partitioning, chemical decomposition, and biodegradation, that need to be considered. Efforts are currently underway at Sandia National Laboratory to apply models for the environmental fate of chemical contaminants, such as pesticides, to explosives. This may give a better understanding of appropriate sampling methods (Refs. 14 and 20).

One can envision looking for trace quantities of explosives in the vapor phase, by solvent extraction from the solid phase, or perhaps collecting solid-phase residue by swabbing threaded joints or other weak spots similar to what is done in airport security. From the mine results, it appears that if there is sample to be had at all, the greatest concentrations would be found in the solid phase, either on the ordnance item itself or sorbed into the surrounding soil. If the mine data are applicable to UXO, no more than low parts per billion quantities are expected in soil samples, and considerably lesser amounts are expected in other phases.

We stress that all the above results are based primarily on research on land mines. Munitions tend to be thick-walled steel structures, and unless the structure is compromised from impact, there is little likelihood of any chemical penetrating the casing. Because there is little known data on explosive residue from UXO, we use what is available from landmine research and note that for ordnance we expect both the initial surface contamination and the rate of release to be no better and quite likely worse. Thus, concentrations in the parts per billion for soil and in the parts per trillion for vapor set a minimum requirement on the instrumentation sensitivity for UXO identification by means of chemical signature. True values could easily be several orders of magnitude smaller.

## **2. Background**

In addition to the source term, the background concentrations of explosives must be considered for some sampling schemes. If vapor or soil-sorbed sample will be used, the level of background contamination will be critical. The environment in which much UXO is found has been the scene of numerous explosions of rounds identical or similar to those that did not explode. One must consider how thoroughly the explosives reacted

during detonation, as well as what potential reaction products remain in the soil that could interfere with detection. Because forensic determination of bomb makeup relies upon the detection of trace quantities of unexploded material, some level of background contamination is expected from exploded rounds, as well as from rounds that did not explode, but sheared open. It is important to know how much unexploded residue is expected and how long unreacted explosive residue would survive in the environment. For example, there could be variability in background concentrations between impact areas not used for 30 years and active ranges.

There have been a few studies of background contamination on impact areas. The Cold Regions Research and Engineering Laboratory (CRREL) has studied soil contamination at an inactive range at Fort Ord and at an active antitank firing range at Canadian Force Base Valcartier, Val-Belair, Quebec (Refs. 21 and 22). The munitions fired in the contaminated areas in Canada were light antitank weapon (LAW) rounds filled with octol (70:30; HMX:TNT). At Fort Ord, some LAW AT rounds were fired, but other munition types were fired as well. The general findings for the two locations were similar. At both sites, there were high concentrations of HMX in the soil, especially near the surface and near the target areas. The maximum concentrations exceeded 1,000 mg/kg (ppm), and concentrations fell off sharply with depth and distance from target. There was great spatial heterogeneity in the concentration profiles: samples taken less than 1 m apart differed in one instance by a factor of nearly 400. Concentrations of TNT, RDX, and AmDNT (a biodegradation product of TNT) were lower, with maxima in the parts per million range, and these compounds were detected only near the surface. Trends were observed with the amount of debris (more debris correlated with higher contamination levels) and the length of time since the impact area was used (longer time elapsed correlated with lower contamination levels). Evidence for a decrease in RDX concentration over time was observed at Fort Ord: 1994 and 1997 studies were compared, and the latter showed lower contamination levels. The large HMX/TNT ratio observed in the soil is attributed to the lower water solubility and slower rate of dissolution of HMX compared to TNT, as well as to the greater tendency of TNT to undergo biotransformation. Finally, it is important to note that the origin of contamination is uncertain: the authors were unable to distinguish between unexploded residue from an exploded shell and leakage from damaged but unexploded shells. In some cases, where the soil concentration of HMX was sufficiently high, the authors proposed that the latter must have been the case.

The few available background studies suggest serious difficulties with using chemical trace detection for UXO identification on impact ranges. If, as we assert, the mine measurements represent an upper limit for the amount of sample available from UXO, then even subparts-per-million background concentrations of RDX and TNT and its associated compounds are problematic. The cited studies do not provide the true values for TNT or RDX concentrations in the concentration profiles of interest; that is, the detection limits for the standard analytical techniques used are in the 0.1 ppm order of magnitude, well above the maximum anticipated signature for unexploded munitions. It appears residual HMX contamination would always be a problem in areas where rounds containing HMX were fired. Finally, there is the spatial heterogeneity of the contamination pattern to consider. Unless hot spots can be attached to leakage from specific ordnance items, this degree of variability in background would likely produce false positives.

### **3. Sampling and Preconcentrators**

If there is an explosive sample to be had, previous work suggests that it is likely to be found in greatest quantity in the solid phase and/or sorbed onto soil particles. This suggests wet chemistry techniques, such as solvent extraction, as a method of sampling. Because ordnance detection does not have the same stringent time line requirements of vapor mine detection, this option seems worth considering.

One common procedure used in analytical chemistry to overcome low sample availability is to employ a preconcentrator. For example, for gas phase samples, large quantities of air contaminated with low levels of a target compound would be drawn through a cryo trap. The components with high vapor pressures at the temperature of the trap would pass through (i.e., at dry ice temperatures, nitrogen, oxygen, and other components of ambient air such as argon would pass through). Target compounds, such as explosives and organic pesticides, which are solids with no significant vapor pressure at these temperatures, would be collected in the trap. The trap would then be reheated to release the concentrated sample for further testing. Of course, this is the simplest of examples. There are more exotic concentrators designed for specialized purposes, using, for example, specialty coated beads, capillaries, or fibers that preferentially adsorb compounds of interest. One commonly used concentrator that is applicable to explosives is the solid phase microextraction (SPME) fiber, which can be coated with various polymers to enhance the collection of trace species.

The main criteria for selecting preconcentrators are the rate and efficiency of both adsorption and desorption and the specificity for target compounds. The most abundant interfering compound in the environment is likely to be water, so preconcentrators should eliminate water to the greatest extent possible. This makes cold trapping at temperatures substantially below room temperature unappealing. Other possible interferers include organic pesticides and fertilizers. Pesticides in particular can have a long lifetime in the environment. Because many are chlorinated hydrocarbons (which, like nitroaromatic explosives, have high electron affinities), they may present potential confusers to some detection methods. A difficulty specific to the detection of explosives would be found in any preconcentrator that required heating to more than about 200 °C to release the sample. Many explosives are unstable in this temperature regime and either decompose or explode (see Table IV-1).

Another method of preconcentration is the tissue sampling used in airports to collect and concentrate solid samples from luggage handles for analysis by explosives detectors. It seems plausible that these techniques could be applied to ordnance, if it is found that substantial surface contamination is present on live fired rounds, either from contamination at the point of manufacture or from transport from the main charge explosive (other sources of explosive release include damage to rounds and migration through threads or other seams). It has been proposed that samples could be concentrated from the soil using laser desorption or water jets to promote vapor formation.

## **B. EPA STANDARD FOR SOIL CONTAMINATION**

As a point of reference, EPA Method 8330 is the standard analytical method for determination of 14 explosives and co-contaminants in soil (Ref. 13). It is designed to test contaminated soil, where regulatory action levels are in the tens of parts per million. EPA 8330 uses HPLC. Soil is extracted with a polar solvent, such as acetone, methanol, or acetonitrile, and filtered. The extraction step is quite time consuming, requiring 18 hours. Then samples are subject to reverse-phase HPLC with a photo-array detector. The usual detection wavelength is in the UV. The method detects TNT, HMX, RDX, TNB, tetryl, DNB, AmDNT, and NT, with detection limits of about 1 ppm or less. If explosives are detected on the primary column, the extraction is resampled for confirmation on a second column. Given the upper bounds on sample quantities predicted above, this method will not be useful for ordnance identification unless orders of magnitude concentration increases can be achieved using preconcentrators.

### C. COLOR TESTS

Wet chemistry tests that give a yes/no answer in the field would be extremely useful. Although color tests are generally sensitive to all compounds of the same family, rather than to a single specific compound, this feature is not likely to be limiting in the identification of explosives. In fact, it may be beneficial if a test is sensitive to TNT and also its closely chemically related breakdown products and manufacturing impurities. For example, a color test for nitroaromatics could be employed. Color tests have been examined as a screening alternative to more expensive laboratory-based, off-site tests now used for contaminated soils. As described above, soils are extracted with a solvent such as acetone, and the chemical color tests are performed. For the TNT test, a strong base (KOH) is added to the extraction product, and if TNT is present, the Janowsky anion, which is red in color, is produced. Absorbance is measured at 540 nm using a field spectrophotometer. CRREL and others have evaluated color tests for TNT, RDX, and DNT. The detection limits all fall in the low parts-per-million range. Thus, these methods are also unlikely to be useful at the expected contamination levels (Ref. 13).

### D. IMMUNOASSAY METHODS

Immunoassay techniques can provide molecule-specific detection through enzyme-catalyzed reactions. For example, there is a monoclonal antibody specific to TNT which can be exploited. Enzyme-linked immunosorbent assay (ELISA) is one such technique that originally was developed for monitoring wastewater at TNT production plants (Refs. 13 and 23). TNT produces a color change that is compared to a standard color chart. ELISA has also been used to detect TNT contamination in soil extractions. Detection limits are in the low parts-per-million to sub parts-per-million concentrations. ELISA also has been adapted for use in detecting TNT residues on hands. The preparation time is fairly quick for soil samples: 3 min shaking with acetone followed by 10 min settling. There are also immunoassay tests to detect RDX (Ref. 13). Again, the detection limits are orders of magnitude above what is expected for UXO, and without considerable preconcentration efforts, immunoassay methods are not likely to be useful.

### E. ION MOBILITY SPECTROMETRY

In ion mobility spectrometry (IMS), the vapor sample is introduced into the spectrometer and ionized, usually using a  $^{63}\text{Ni}$  source. The ions enter an electric field region, where they drift upstream against a flow of gas at ambient pressure. Ion current is measured as a function of drift time. Species selectivity is dependent on time of flight in

drift area for various ions. IMS has high sensitivity to organic substances with electron capturing groups, such as the nitro groups on nitroaromatics (Ref. 24). IMS has a detection limit of picogram to nanogram quantities for common explosives: 2 ng has been reported for PETN and 200 pg for RDX.

IMS instruments are commercially available (Ref. 24) and are used for airport security, among other applications. Sampling for airport security is done by taking tissue swabs from luggage handles, for example. The material on the swab is vaporized and introduced into the IMS. The Barrington Ionscan is one currently available instrument. It has a 5-sec processing time and is made up of two modules.

The task of this system in the airport environment is limited to detecting trace quantities of explosives in a relatively clean and otherwise explosive-free environment. Some modification of sample collection procedures would be required for UXO identification in a less controlled environment. Swabs could be used if surface contamination is found to be a reliable sample source. Alternatively, solvent extraction of soils or vapor concentration could be considered. In either case, in a less controlled and more contaminated environment, some care must be taken with the sampling. IMS has limited dynamic range, and competitive ionization of interfering species can suppress analyte ion formation (Ref. 25). In addition, water can decrease the intensity of response and add interfering reactant peaks in areas of interest.

Optimizing an IMS system to detect a large matrix of explosive compounds may not be trivial. The optimal temperature and carrier gas can vary greatly for different analytes. Dopants in the carrier can increase response strength for some analytes but may have an adverse effect on detecting others. The more complex chemistry may also clutter the spectrum. For example, in one study, different optimum conditions were observed for TNT, RDX, and PETN (Ref. 26).

The sensitivity of IMS for explosives can be quite high. A commercial IMS detecting vapor in air has demonstrated a detection limit for RDX reported at 0.3 ppt ( $3 \text{ fg/cm}^3$  in a flow of  $3 \text{ cm}^3/\text{sec}$ ). With a quartz tube preconcentrator, the sensitivity can be increased by a factor of 10. These sensitivities approach sample levels that have been reported for landmines. Of course, as stated above, it remains to be determined that these levels are applicable for UXO (Ref. 23).

## F. GAS CHROMATOGRAPHY

In gas chromatography (GC), a sample is vaporized and introduced into a heated separation column. The column is packed with a substance such as specially coated glass beads that will differentially adsorb different materials. The retention time of various molecules in the column is a complex function that will depend on the strength of their interaction with the packing material, the carrier gas, its flow rate, and the column temperature. Ordinary GC columns are physically long (meters) and by design have long retention times (minutes) to attain the greatest possible separation of analytes in mixed samples, as well as to enhance the degree of specificity for identifying a particular analyte by its retention time under known experimental conditions (carrier gas, flow rate, temperature, etc.).

There are several difficulties using GC to detect explosives. Some explosives are too involatile to use. Alternatively, the high temperature of GC can degrade thermally sensitive explosives. Strong adsorption of some explosives onto the stationary phase in the column affects elution and can degrade the performance of the column. Also, contamination from the environment can foul the column and degrade its performance. For applications that require quick yes/no answers about the presence of a particular analyte, GC can be too slow. An adaptation called fast GC uses short columns and high gas flow rates to increase speed, but at the cost of decreased resolution and specificity (Ref. 16).

Traditional GC uses a flame ionization detector (FID), which is not very sensitive to explosives. The FID detects carbon; dilution of the carbon content with nitrogen or oxygen decreases the sensitivity (Ref. 23). Two alternatives are the electron capture detector (ECD) and chemiluminescence detectors, which can readily detect military explosives:

- *Electron capture detector.* ECD is very sensitive to chlorides, esters, and nitro compounds and is commercially available. Selectivity in complex examples with large amounts of accompanying substances is low, and sensitivity for other compounds is high (Ref. 23). Sensitivities at the picogram level have been demonstrated for EGDN, NG, TNT, DNT, RDX, PETN, tetryl and HMX.<sup>17</sup>

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<sup>17</sup> For sample preparation, it would be fairly standard to extract a 2-g sample of soil with 10 mL of solvent and use 100  $\mu$ L for the injection volume into the column. This procedure, if there are no further dilution steps, would translate picogram detection limits to 0.05 ppb concentration of analyte in the original soil sample.



- *Chemiluminescence.* Chemiluminescence detection is based on the formation of nitrogen oxide by high-temperature pyrolysis of compounds containing nitro groups. The NO is exposed to ozone, and the resulting reaction forms excited NO<sub>2</sub>, which spontaneously emits a 600-nm photon. Chemiluminescence detectors are commercially available, and the technique has been successfully used in forensics labs for the detection of explosive residues. The system can suffer false positives from other nitroaromatic compounds (Ref. 23), but this should not be a serious limitation for the proposed application. Sensitivities for explosives are in the low picogram range.

## G. ELECTRON CAPTURE DETECTION WITHOUT GC SEPARATION

By directly introducing the sample into the detector, it is possible to exploit the sensitivity of ECD to nitroaromatics without the long time required for GC separation. Success for this technique rests on the ability to discriminate explosives of interest from other confuser molecules, because the procedure no longer benefits from a prior separation step. As noted above, ECD can be highly sensitive to compounds other than the target analytes. Laboratory research at the University of Missouri, Rolla, has shown ability to use a back-to-back ECD set up to uniquely identify DNT (Ref. 27). The most common interferents with high electron affinities are chlorinated aromatics (i.e., pesticides). These are more stable to electron bombardment than nitroaromatics. So, two detectors are separated by the electron bombardment region. The first detector encounters and detects all electron-capturing molecules, but the second encounters only the more stable chlorinated compounds. Thus, these can be screened out. In laboratory setting, with a thermal concentrator, sensitivities in the subpicogram range have been achieved.

## H. MASS SPECTROMETRY

Mass spectrometry (MS) is a widely used analytical chemistry technique for the detection and identification of chemical compounds. The sample of interest is introduced into an evacuated chamber and ionized. In the usual ionization process, the positive ion of the analyte is formed, and a number of "daughter" ions from fragmentation of the parent species are also formed. These ions are separated by their mass-to-charge ratio in one of several ways. In a TOF instrument, separation takes place in the time required for the various ions to traverse a drift region. In a quadrupole instrument, separation takes place by the differential bending of the different ion trajectories in a quadrupolar electric field region.



MS is a sensitive technique that has been used in the detection of explosives. For example, an atmospheric pressure inlet TOF-MS was found to have 10-fg sensitivity for TNT. Although field-portable TOF-MS exist, some of these instruments require substantial support in high-speed vacuum pumps. The pumping speed requirement will depend on the sampling system and its attendant gas flow load. In addition, MS is often preceded by a separation step, for example GC. If this is not done, then the mixture of ions formed may present an uninterpretable clutter of returns to the detector (Ref. 23).

## **I. LASER FRAGMENTATION SPECTROSCOPY TECHNIQUES**

Laser induced fluorescence (LIF) has been used for the detection of explosives in contaminated soil, such as that found at ammunition plants. The first step is to photodissociate TNT to form  $\text{NO}_2$ , which absorbs a 226-nm photon. The excited state of  $\text{NO}_2$  rapidly predissociates to form NO. The NO absorbs another 226-nm photon, and undergoes a resonant transition to an electronically excited NO state, which fluoresces. The 226-nm photons are produced by mixing a tripled YAG (yttrium, aluminum, garnet) laser with a YAG-pumped dye laser. The LIF spectrum is recorded by scanning the dye laser. The LIF intensity is related to the concentration of the analyte, in this case TNT.

This is a fairly elaborate experimental set-up, using two lasers, lots of optics, and a vacuum system, which raises questions of fieldability. If samples could be tested off-site in a laboratory, however, it is a potentially sensitive technique. Experiments performed at Mississippi State University found the detection sensitivity under the conditions tested was 4 ppm by weight in soil. Extrapolating from this result, it is estimated by the University that the ultimate detection limit that could be achieved with this apparatus is 40 ppt (Ref. 28). This detection limit is consistent with similar experiments at the Army Research Laboratory, which show detection limits for TNT and RDX of 24 and 8 pg, respectively, using TOF-MS detection (Ref. 29).

## **J. FM INFRARED SPECTROMETER**

Infrared spectrometry can be used to detect nitrogen-containing decomposition products. TNT, RDX, or PETN vapors can be catalytically decomposed. The fragments are desorbed for analysis with a frequency-modulated, mid-IR, tunable diode laser. In experiments at Stanford Research International (SRI), fragments were detected at parts-per-trillion levels; it is estimated that sub-picogram levels of explosives can be detected (Ref. 30). Application issues include sample handling and the overhead of liquid-nitrogen-cooled diode lasers and vacuum lines. Because the technique detects fragments,

it lacks specificity and can suffer interference from related species containing the same functional groups. In addition, the catalyst presents some difficulties. Debris from soil can degrade its performance, it can have substantial recovery times, and  $N_2$  and  $O_2$  can be catalytically converted to form an analyte species,  $N_2O$ .

#### **K. SURFACE-ENHANCED RAMAN SPECTROSCOPY**

Surface-enhanced Raman spectroscopy (SERS) is a technique with the potential for both high sensitivity and high specificity. The Raman effect is an inelastic scattering phenomenon, where a photon collides with a molecule and loses some of its energy to the molecule. The molecule can accept energy only in quantized amounts, determined by its vibrational and rotational energy levels. The wavelengths of the scattered photons and the incident photons differ by these transition frequencies, resulting in a spectrum that is unique to the molecule. A laser at higher energy than the infrared frequency of the desired vibrational transitions is used to pump the process, and the resulting scattering is observed in the direction orthogonal to the incident beam.

The intensity of the Raman spectrum can be enhanced considerably (by 6 to 8 orders of magnitude) if the analyte is adsorbed onto a specially treated surface. The molecule interacts with the surface to enhance certain vibrational modes. Compounds can be detected in the low parts-per million to parts-per-billion range, with mass detection limits in the picogram level. In one experiment, sensitivity in the picomole to femtomole range was obtained for TNT adsorbed on colloidal Ag or Au. In experiments at MIT, a near-IR laser with  $13\text{ cm}^{-1}$  resolution was used, and the required accumulation times were 1 to 40 sec. A SERS spectra has been obtained from about 1 pg TNT sampled as  $5 \times 10^{-9}\text{ L}$  of  $10^{-7}\text{ M}$  solution (Ref. 31). In addition, SERS has the potential to detect chemical warfare agents, if trace signatures are available. SERS spectra for nerve agent simulants DMMP and DIMP have been observed using roughened silver oxide substrates at Oak Ridge National Laboratory (Ref. 32).

#### **L. POLYMERS**

Numerous polymer-based techniques have been developed or proposed for the detection of trace quantities of environmental contaminants in the vapor phase. This is a primary focus of the DARPA dog's nose program. These schemes in general do not employ a single polymer that uniquely adsorbs a particular molecule of interest. Rather, they rely on an array of polymers that differentially adsorb a variety of molecules, some of which are of interest. Specific chemicals are identified by a fingerprint defined by their

relative adsorption on the array of polymers. A variety of methods, described below, are used to detect the loading of molecules on the polymer arrays.

Explosive compounds, nearly all of which contain nitro groups ( $-\text{NO}_2$ ), are good candidates for detection with polymer techniques. For example, in all nitro compounds, and particularly in nitroaromatics, the  $-\text{NO}_2$  groups are electron-rich sites. Polymers with complementary electron-poor sites can be selected for detectors sensitive to explosives. Of course, nontarget compounds with similar electrostatic properties may also be attracted to the polymers.

To develop a practical polymer-based detector, requirements specific to the polymer must be met. For the detector to continue to function beyond the first detection, the adsorption process must be reversible. The time constants for both adsorption and desorption must be rapid, at least in comparison to the requirement for the sampling rate. Further, the polymer must be robust with respect to other common molecules. Water, being ubiquitous, can be a particular interference problem. If it is strongly adsorbed to the polymer, sensitivity and selectivity for molecules of interest can be greatly reduced. Work in the identification of appropriate polymers for the detection of explosives is an active area of research.

## **1. Surface Acoustic Waves (SAWs)**

For measurement of surface acoustic waves, quartz resonators are coated with selected polymers. As the analyte molecules adsorb onto the polymers, mass changes induce frequency deviations in the oscillating resonators. For example, in one study, a 250-MHz cut-quartz resonator device was coated to provide frequency shift of 250 kHz upon loading of nitroaromatics. In this laboratory study, the detector response time was 4 sec. The detection limits extrapolated by the authors from the lab results were 235 ppt and 3 ppb for 2,4-DNT and NB, respectively (Ref. 33). This technique is currently in laboratory and early field tests. Routine application of this technique to detection of explosives in the field will require substantial technical and engineering advancements.

## **2. Thin-Film Resonators**

The sample can also be passed over an array of bulk acoustic sensors coated with polymers sensitive to explosives. A bulk wave acoustic resonator is formed by a thin metal coating on each side of piezoelectric slab, which can be used to excite the resonance. The resonance frequency depends on thickness of the cavity, as well as mass loading. If material is adsorbed by the coating, the resonant frequency will change.

Detection of TNT has been demonstrated at the 5-ppb level in the laboratory by a group at Rockwell (Ref. 34).

### **3. Polymer Composite Arrays**

Vapor loading can also be measured by monitoring resistance changes in a polymer composite array. Adsorption of the vapor causes swelling of polymeric phase of the composite, which increases electrical resistance of the composite. It is desirable that the resistance change is linear, reproducible, and reversible. Laboratory research at the California Institute of Technology with a carbon black composite for straight chain alcohols and alkanes has achieved detectability in the parts per thousand level (Ref. 35). Field application of this technique to detection of explosives will require advances that increase sensitivity and expand the potential analytes.

### **4. Dye/Optical Detection**

Detection can also be accomplished by exploiting polymer-immobilized dye molecules. Nile red has shown different fluorescent response patterns (spectral shifts, intensity changes, spectral shape variations, and temporal responses) after exposure to organic vapors. Responses depend on size, shape, polarity (i.e., physical and chemical properties) of the vapor, and the polymer (Refs. 36, 37). Laboratory experiments at Tufts University with fiber-optic bundles have shown proof of concept, demonstrating sensitivity in the 1,000 ppm range; however, this was not an attempt at ultimate sensitivity. Field application of this technique to detection of explosives will require substantial technical advancements.

### **5. Fluorescence Detection**

Nomadics Corporation, in collaboration with Professor Tim Swager at MIT, has developed a detector based on a fluorescent polymer (Ref. 38). The polymer is customized for binding to nitroaromatics. It fluoresces continuously in its unbound state, but if a nitroaromatic compound binds to it, the fluorescence is quenched. The technique shows very high sensitivity, with limits demonstrated in the tens of femtograms. The specificity is moderate: any nitroaromatic will bind to the polymer as a charge transfer complex. Other molecules that present similar lowest unoccupied molecular orbitals to form charge transfer complexes could also bind to the polymer. In tests, water has presented some difficulties.

## M. CANINE

The ability of dogs to detect explosives is well known. We are not aware of any attempts to test trained dogs on ordnance; their use is typically limited to landmine and terrorism applications. These related efforts can give an indication of the levels of contaminants that dogs are able to detect and their reliability; however, note that there is no consensus on what analyte(s) dogs detect—whether it is the explosive or some manufacturing impurity or breakdown product. There is some evidence that detection is through a secondary signature. Therefore, extrapolation of results from dogs can be more problematic than for other techniques. If a target explosive is manufactured differently from a test explosive, test data may simply not be applicable.

Results of published tests vary considerably. For security reasons, the quantities of explosives used in aircraft tests are often not revealed, so they can be difficult to interpret. In one test conducted in Canada, dogs detected about 70 percent of target explosives. This test was conducted using a very small number of dogs and explosives (41 hidden explosives in 14 passes) (Ref. 39). A small test on spiked luggage indicated the sensitivity of dogs is in the tens of parts-per-trillion range for the compounds tested<sup>18</sup> (Ref. 39).

## N. MICROBIAL BIOSENSORS

Microorganisms are known to adapt in the presence of a contaminant so that it can be exploited as a nutritional source. The hope of this line of research is that these populations could be tagged so that their concentration in contaminated environments could be monitored. Current experiments are aimed at understanding the microbial populations in explosives-contaminated soils (Ref. 40).

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<sup>18</sup> Note that, unlike most military explosives, two of the tested explosives, dynamite and C-4, contain compounds with substantial vapor pressures under ambient conditions.

## V. CONCLUSIONS

1. At present, no technique exists for the routine field identification of ordnance fills. X-ray radiographs can and do provide information on the structure of the munition, which can be useful in deducing its contents and condition; however, X rays will not provide definitive identification of chemical composition.
2. Neutron techniques, exploiting either inelastic scattering, thermal neutron capture, or both, are promising for determining elemental composition. In tests, these techniques have achieved good success identifying chemical warfare agents and moderate success detecting explosives. The difficulty for explosives identification is the relative insensitivity to nitrogen, which has a small thermal neutron capture cross section and is not a strong inelastic scatterer of fast neutrons. In addition, detection of N by means of TNA is hampered by interference from a neighboring Si  $\gamma$ -ray peak. Current efforts may improve sensitivity to nitrogen, however, and should continue. There is no reason at this time to discount neutron techniques for identification of munition fills, including explosives.
3. Data for evaluating acoustic techniques for filler identification are limited but promising. Current systems have performed reliably against a limited array of known munitions and fills, with the primary emphasis on detecting chemical warfare agents. More work will be required to explore the applicability of acoustic technology to a wide variety of munitions, with various degrees of damage and degradation, and concentrating on identification of high explosives.
4. For chemical trace detection, there is a need to establish whether there is a chemical signature for fired, unexploded munitions and to better characterize the background residue in both densely contaminated impact areas and in less contaminated areas such as safety zones. Data on both quantities is very limited. Our conclusion based on current data is that the largest possible values for the source term will be in the parts per billion for sample sorbed onto the soil and in the parts per trillion for vapor samples. True values could easily be several orders of magnitude lower. Background contamination in the parts per billion to parts per million ranges has been observed on ranges. For ease of use, vapor sniffing is the most appealing approach. Because there is no need to do instantaneous vapor-phase-only detection for the UXO cleanup

mission, however, it is worth considering the more traditional chemistry techniques used in environmental monitoring and forensic analysis, some of which currently offer very high sensitivity. Since most of the mass fraction of the explosive is sorbed onto the soil, the possibility of detecting analytes in the soil adjacent to the round should not be discounted. In addition, the applicability of swabbing excavated rounds should be explored, although initial results on surface contamination of UXO are ambiguous at best. If the source and background terms are favorable, there is ongoing work to understand the behavior of the explosives in the environment and to develop sensitive techniques for chemical detection. Table V-1 summarizes the detection limits achieved or expected for the traditional and emerging techniques considered. For most emerging techniques, ultimate detection limits under field conditions have not been established; this must of course be a priority if source terms are favorable.

**Table V-1. Summary of Trace Detector Limits**

Technique	Phase	Explosive	Detection Limit
EPA 8330	Soil extraction	TNT, HMX, RDX, TNB, tetryl, others	<1 ppm
Color tests	Soil extraction	TNT, RDX,DNT	Low ppm
Immunoassay	Soil extraction	TNT	Low or sub ppm
IMS	Vapor/Soil extraction	TNT, RDX, PETN	0.3 ppt
GC/ECD	Vapor/Soil extraction	Nitro-organics	ppt
GD/chemiluminescence	Vapor/Soil extraction	Nitro-organics	ppt
ECD	Vapor/Soil extraction	Nitro-organics	<ppb
MS	Vapor/Soil extraction	All	fg
LIF	Vapor	TNT	40 ppt (est.)
FMIR	Vapor/Soil extraction	TNT,RDX,PETN	ppt
SERS	Soil extraction	TNT	pg
Polymer/SAW	Vapor	Nitroaromatics	<ppb
Polymer/TFR	Vapor	Organic compounds	>ppm
Polymer/Dye	Vapor		>ppm
Canine	Unknown	Uncertain	~10 ppt
Microbe	Soil		

## ACRONYMS

ACE	Army Corps of Engineers
AmDNT	aminodinitrotoluene (isomer as specified)
AT	antitank
BGO	bismuth germanate
BIP	blow in place
CCD	charge-coupled device
CRREL	Cold Regions Research and Engineering Laboratory
CW	chemical warfare
D-T	deuterium-tritium
DARPA	Defense Advanced Research Projects Agency
DNB	dinitrobenzene (isomer as specified)
ECD	electron capture detector
EGDN	ethyleneglycol dinitrate
ELISA	enzyme-linked immunosorbent assay
EMI	electromagnetic induction
EOD	Explosive Ordnance Disposal
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
fg	femtogram ( $10^{-15}$ g)
FID	flame ionization detector
FMIR	frequency modulated infrared
FNA	fast neutron analysis
GB	sarin
GC	gas chromatography
HE	high explosive
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane
HPGe	high-purity germanium
HPLC	high-performance liquid chromatography
INEEL	Idaho National Engineering and Environmental Laboratory
IMS	ion mobility spectrometry
LAP	load and pack
LAW	lightweight antiarmor weapon
LIF	laser-induced fluorescence



MS	mass spectrometry
NAA	neutron activation analysis
NG	nitroglycerine
NQR	nuclear quadrupole resonance
NT	nitrotoluene (isomer as specified)
PELAN	pulsed elemental analysis with neutrons
PETN	pentaerythritol tetranitrate
PFNA	pulsed fast neutron analysis
pg	picogram ( $10^{-12}$ g)
PINS	portable isotopic neutron spectroscopy
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
SAW	surface acoustic wave
SERDP	Strategic Environmental Research and Development Program
SERS	surface-enhanced Raman spectroscopy
SPME	solid phase microextraction
SRI	Stanford Research International
TFR	thin film resistor
TNA	thermal neutron activation
TNB	trinitrobenzene (isomer as specified)
TNT	2,4,6-trinitrotoluene
TOF	time of flight
TOF-MS	time-of-flight mass spectrometer
UV	ultraviolet
UXO	unexploded ordnance
VX	nerve agent
WP	white phosphorus
YAG	yttrium aluminum garnet

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